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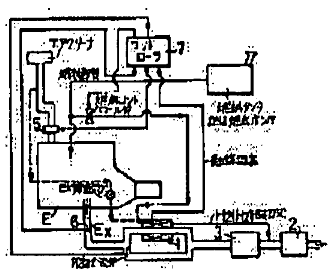
(54) NITROGEN OXIDE REDUCING DEVICE FOR INTERNAL COMBUSTION ENGINE

(57)Abstract:
PURPOSE: To deoxidize and purify the NOx in the exhaust gas directly by the H2 from a hydrogen generator under the exhaust gas low temperature ambiance so as to reduce the NOx, by composing the system to make a part of a hydrocarbon fuel converted into a hydrogen gas to feed by a reformer catalyst converter.
CONSTITUTION: H2 is fed near the entrance of a deoxidizer catalyst 2. The air amount is measured by a suction air amount sensor 5 of an engine E to make the H2 to feed at the same level with the NOx in the exhaust gas. The NOx density in the exhaust gas is found by an NOx sensor 6, and after the NOx flow is calculated from the outputs of both sensors 5 and 6 in a controller 7, the fuel flow led in a reformer catalyst converter, and the reformer catalyst converter temperature by an exhaust gas flow dividing valve 11, and also an air valve 12 for reforming in the system to carry out a partial oxidization, are controlled in order to generate the H2 corresponding to the NOx flow.



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CLAIMS

[Claim(s)]
[Claim 1] While forming the catalyst equipment for carrying out catalytic reaction of hydrogen gas and the nitrogen oxides to nitrogen oxides within the basis of the existence of oxygen gas, and an exhaust system, and decomposing into nitrogen gas and water during exhaust air by combustion of the fuel supplied from the fuel supply system in an internal combustion engine's combustion chamber The hydrogen generator which generates hydrogen with a reforming catalytic converter for some hydrocarbon fuels, such as a methanol or LPG, and natural gas, to the entrance side of this catalyst equipment is formed. Nitrogen-oxides reduction equipment of the internal combustion engine characterized by constituting possible [supply of hydrogen gas], carrying out direct reduction purification of the nitrogen oxides under said exhaust air with the hydrogen gas from this hydrogen generator under the exhaust air low-temperature ambient atmosphere in near the silencer of an exhaust system, and reducing these nitrogen oxides.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] without it spoils the goodness of the fuel consumption of the engine concerned in the so-called lean burn engine and the so-called diesel power plant which this invention requires for an internal combustion engine's nitrogen-oxides reduction equipment, and use a lean mixture especially and aim at the improvement in fuel consumption, other hydrogen fueled engines, etc. -- the concentration of the oxygen gas under exhaust air (the following O2 is called) -- Lean NOX who can do reduction purification of the nitrogen oxides (Following NOX is called) effectively regardless of how It is related with a catalyst exhaust-air purification system.
[0002]
[Description of the Prior Art] An internal combustion engine and NOX according [in / mainly / a piston engine] to the former and a ** three way component catalyst in the reduction approach of the nitrogen oxides (Following NOX is called) exhaust air Use ** Lean NOX of a decreasing method ** super-rarefaction air-fuel ratio NOX by the catalyst The decreasing method (for example, JP,1-139145,A)
Three ** are considered. However, the weight ratio of the fuel with which the approach of ** is supplied to an engine, and air must be about 14.5, i.e., theoretical air fuel ratio. It is NOX if a fuel uses a thin air-fuel ratio from theoretical air fuel ratio. It does not decrease. However, it is known that considering the economical efficiency of fuel consumption the direction which operated the engine by the rarefaction side has less specific fuel consumption than theoretical air fuel ratio as shown in drawing 2 , and it is efficient.
[0003] Next, ** is NOX by the so-called lean burn engine. It is going to reconcile reduction and fuel consumption reduction. However, NOX If it is going to use the air-fuel ratio which can be reduced enough, engine fuel consumption not only worsens, but it will approach the flame-failure limitation of combustion and a dry area and drivability will worsen [operation]. In order to prevent this, turbulence and the increment in the rate of flow are measured with the air flow in a cylinder, the rate of combustion is made quick and there are some which are going to improve a flame-failure limitation so that it may become a thin region more. However, if air turbulence and the increment in the rate of flow are performed too much, since the flame nucleation at the time of ignition and the flame propagation in early stages of combustion will be barred on the contrary, there is a limitation in expansion of the flame-failure limitation by this approach. Moreover, it is Generating NOX, if a flame-failure limitation moves to a rarefaction side more as shown in drawing 3 although there is also the approach of making it into the rich mixture to which the air-fuel ratio distribution in a cylinder was adjusted, and it was suitable for ignition only near the ignition plug. Since the rate which decreases decreases as the broken line showed, big effectiveness is not expectable.
[0004] ** In order to compensate the fault of the above-mentioned **, operate using near [a little near theoretical air fuel ratio] the specific-fuel-consumption minimum point from a flame-failure limitation, and it is NOX with a little insufficient reduction. Zeolite system Lean NOX It is going to purify with a catalyst. This approach may become a fuel-efficient system. However, this

Lean NOX A catalyst is a lot of O2 during exhaust air. It is NOX under existence. It will return, temperature conditions etc. are severe and it is NOX of catalyst sufficient in the present condition. There is a problem which should be solved practically that the rate of purification and endurance can be easily incompatible. It is NOX, using the air-fuel ratio which can make engine specific fuel consumption small as much as possible as mentioned above. The approach of reducing enough all has many practical problems.
[0005] By the way, it is an excess O2 during exhaust air also at a lean burn engine or a diesel power plant. Although containing is fundamentally the same, exhaust air of this engine is O2 during exhaust air. It is O2, so that it contains and a lean mixture is used. Concentration becomes large. Such O2 NOX under exhaust air to include He is Lean NOX about the catalyst which performs reduction purification. It is called a catalyst and the catalyst of a noble-metals system, for example, a zeolite system, is used in many cases. This Lean NOX At a catalyst, it is NOX. The relation between the rate of purification and temperature shows drawing 4 . And a pyrosphere 350 degrees C or more is mainly HC-NOX. It is a reaction. A low-temperature region 250-350 degrees C or less is NOX. H2 It becomes the reduction reaction to depend and is NOX. It can purify.
[0006] However, Lean NOX Since an exhaust-gas temperature amounts also to a maximum of 800-900 degrees C since a catalyst is installed near an engine exhaust manifold, and, as for exhaust air of a lean burn engine, an air-fuel ratio uses a rarefaction side from theoretical air fuel ratio, it is H2 during exhaust air. It hardly exists. Therefore, the property by the side of low temperature was the field which cannot be used conventionally.
[0007]
[Problem(s) to be Solved by the Invention] The purpose of this invention is what solves the above-mentioned conventional various problems. a lean burn engine -- or -- always -- O2 -- under exhaust air of the diesel power plant operated by the excess (air) side -- NOX O2 Without spoiling the goodness of the fuel consumption of a lean burn engine or a diesel power plant under coexistence O2 under exhaust air concentration -- how -- not asking -- NOX Exhaust air, purification system, i.e., NOX, which carries out reduction purification effectively NOX of the internal combustion engine which can control a burst size It is going to offer reduction equipment.
[0008]
[Means for Solving the Problem] NOX of the internal combustion engine of this invention Reduction equipment is NOX during exhaust air by combustion of the fuel supplied from the fuel supply system in an internal combustion engine's combustion chamber. O2 The basis of existence, It is H2 within an exhaust system. NOX Catalytic reaction is carried out and it is NOX. While forming the catalyst equipment for purifying The hydrogen generator which generates hydrogen with a reforming catalytic converter for some hydrocarbon fuels, such as a methanol or LPG, and natural gas, in the entrance side of this catalyst equipment is formed, and it is H2. It constitutes possible [supply]. It is H2 from this hydrogen generator under the exhaust air low-temperature ambient atmosphere in near the silencer of an exhaust system. NOX under said exhaust air Direct reduction purification is carried out and it is this NOX. It is the reduced configuration.
[0009]
[Function and Effect] NOX of the internal combustion engine of this invention which consists of the above-mentioned configuration Reduction equipment does the following operations so.
[0010] Namely, NOX of the internal combustion engine of this invention which this invention person etc. invented Reduction equipment By considering as a configuration as shown in drawing 1 , it is NOX during exhaust air by combustion of a supply fuel in an internal combustion engine's combustion chamber. O2 The basis of existence, H2 NOX Carry out catalytic reaction and to the entrance side of nitrogen gas and the catalyst equipment formed in the exhaust system decomposed into water A methanol or LPG, Some hydrocarbon fuels, such as natural gas, are led to a reforming catalytic converter, and it is H2. H2 from the hydrogen generator to generate It supplies. the bottom of the exhaust air low-temperature ambient atmosphere in near the silencer of an exhaust system -- this -- H2 NOX under said exhaust air efficient -- exact -- direct

reduction purification -- carrying out -- this NOX The operation effectiveness to reduce is done so. For this reason, NOX of the internal combustion engine of this invention For reduction equipment, an engine operating air-fuel ratio is O2 a rarefaction side and under exhaust air in theoretical air fuel ratio from a rich side, theoretical air fuel ratio, and theoretical air fuel ratio. Existence or O2 Regardless of concentration, it is NOX. Since it can decrease according to a catalyst, it is the engine (automobile) engine-performance top and fuel consumption top NOX. The profitableness which can choose an optimum value, without taking reduction conditions into consideration can be given.
[0011]
[Example] A reforming catalytic converter is classified according to the fuel which uses the hydrogen generator in an example for an engine as follows.
[0012] namely, -- if it is in the engine which uses a methanol as a fuel -- 1 -- the gas which carried out heating evaporation of the methanol with exhaust air using transition metal catalysts, such as Pd, Pt, and Cu/Cr/nickel, -- this catalyst -- leading -- H2 It generates. About 300 degrees C of catalyst inlet gas temperature are best, and the reaction at this time is [0013].
[Formula 1]
$$CH_3OH \rightarrow CO + 2H_2$$

[0014] It becomes.
[0015] 2) Make a methanol steam mix air, carry out partial oxidation of some methanols according to Cu-nickel-Cr/alumina catalyst, and it is H2. It generates. 400 degrees C - 500 degrees C are suitable for temperature, it controls the air flow rate made to mix in a methanol, and maintains temperature. The reaction in this case is [0016].
[Formula 2]
$$CH_3OH + Air \rightarrow H_2 + CO + H_2O$$

[0017] It becomes.
[0018] 3) Cu-Mn or Cu-Zn is used for a catalyst, and add a steam to a methanol, or add air and methanol water, and perform steam reforming. About 250 degrees C is suitable for temperature, and a reaction is [0019].
[Formula 3]
$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

[0020] It becomes.
[0021] Moreover, if it is in the engine using hydrocarbon fuels, such as LPG and natural gas, nickel, CO, and Rh are used as a catalyst and it reforms at the temperature of 300-800 degrees C. In the case of this hydrocarbon fuel, the water from a steam, air, or a water tank is added, and reforming is carried out to it. (Temperature changes with catalysts.) There is much methane at low temperature and there is much CO at an elevated temperature. As a reaction, it is [0022].
[Formula 4]
$$HC + H_2O \rightarrow H_2 + CH_4 + CO_2 \quad 300\sim500℃$$
$$HC + H_2O \rightarrow H_2 + CO + CO_2 \quad 800℃$$
$$HC + Air \rightarrow H_2 + CO \quad 800℃$$
$$HC + 排気 \rightarrow H_2 + CO \quad 700℃$$
（ＥＧＲ改質）

[0023] It becomes.
[0024] Moreover, NOX of the internal combustion engine of this example Reduction equipment is NOX with which the exhaust pipe of said exhaust system is equipped. The output of a sensor 6 and the inhalation air content sensor 5 to NOX A flow rate is computed and it is always proper H2. It can also consider as the configuration which controls the air content and reforming fuel quantity in the case of performing the engine exhaust air flow rate or partial oxidation which

determines an amount and heats the reforming catalytic converter as said hydrogen generator.
[0025] Furthermore, NOX of the internal combustion engine of this example Reduction equipment possesses the sensor which can detect the service condition in internal combustion engines, such as injection quantity of the jet pump as rotational frequency, inlet-pipe negative pressure, inhalation-of-air throttle valve opening, or fuel supply system of the internal combustion engine concerned, and is NOX from the output of the sensor concerned. It can also consider as the configuration made into the learning-control method which controls the fuel quantity which carries out the prediction operation of the flow rate, and is supplied to the reforming catalytic converter of said hydrogen generator.
[0026] And NOX of the internal combustion engine of this example It sets to the entrance side of said catalyst equipment, and reduction equipment is H2. Since mixing of exhaust air is made into homogeneity, a mixer can be provided or it can also consider as the configuration which uses the silencer of an exhaust system effectively.
[0027] If it explains in full detail, it will be NOX of the internal combustion engine of this example. Reduction equipment was invented in order to solve said conventional problem, and it shows the basic block diagram to drawing 1 . That is, the 1st point of this example is this H2. It is that reduction uses it in all the operating ranges of Engine E by the exhaust air low temperature side. The 2nd point is H2 in a configuration system, in order to enable use by the side of low temperature. It is incorporating a generator 1. The 3rd point is the operational status of Engine E, or NOX under exhaust air. It is H2 by the amount. A generator 1 is controlled and it is always NOX during exhaust air. It is equivalent extent or superfluous H2 at a mol. It is enabling it to supply.
[0028] A reduction catalyst 2 is H2 when exposed to an elevated temperature. O2 It reacts and is H2-NOX. Since selectivity is lost, it arranges near a silencer 3 so that it may not be exposed to 350 degrees C or more. And this example branches from a fuel line, minds a flow rate control valve, and is H2. Introductory reforming of the fuel is carried out at the reforming catalytic converter as a generator, and it is H2. It is made to generate. H2 It supplies near the inlet port of a reduction catalyst 2. H2 to supply NOX under exhaust air In order to make it equivalent extent by the mol, an air content is measured by the inhalation air content sensor 5 of Engine E. NOX under exhaust air concentration -- NOX a sensor 6 -- 4s ** -- asking -- a controller 7 -- the output of both the sensors 5 and 6 to NOX After calculating a flow rate NOX H2 corresponding to a flow rate It is the configuration which controls the air valve for reforming by the fuel flow introduced into a reforming catalytic converter in order to make it generate, and the thing which performs reforming catalytic-converter temperature by the exhaust air flow dividing valve, and partial oxidation.
[0029] Setting to drawing 5 , an axis of abscissa is NOX. H2 receiving A delivery late and an axis of ordinate are NOX. The rate of reduction (rate of purification) is shown. NOX It receives and is equivalent H(mol) 2. It will be NOX if it supplies. H2 The thing, then NOX which are mixed completely Reduction purification is carried out altogether (theoretical value). However, since complete mixing is not carried out in fact, the rate of reduction becomes like an experimental value. Although there is a part to which the rate of purification is good from the theory in the experimental value, the steam under exhaust air decomposes this on a noble-metals system catalyst, and it is H2. It is because it has changed. Therefore, H2 supplied Many H2 NOX It reacts.
[0030] As other examples, it is H2. NOX which performs reduction purification to depend It sets to reduction equipment and is H2 to the entrance side of a reforming catalytic converter. It can consider as the function to install the mixer which carries out mixed mixing of exhaust air. Moreover, NOX of others of this example Since the hydrogen generator and catalyst equipment which are a purge have a respectively suitable actuation temperature requirement, a reduction catalyst can be installed in the inside of the muffler to which exhaust air expands and temperature falls at 200 degrees C or less, or its lower stream of a river again in the latter part of the oxidation catalyst which installed the hydrogen generator in the outlet of an exhaust manifold in an internal combustion engine's exhaust system.
[0031] Furthermore, as other examples, it is H2 of a hydrogen generator. It supplies and is O2.

NOX under engine exhaust air under coexistence NOX which carries out reduction purification In reduction equipment, it has a means to oxidize HC, such as an oxidation catalyst, a three way component catalyst, and an exhaust air reactor, and CO near an engine exhaust manifold, and he is Lean NOX. It can consider as the configuration which uses Pt-zeolitic catalyst for the reforming catalytic converter as a catalyst. Moreover, a silencing effect can be given to a reforming catalytic converter and a reforming catalytic converter and an exhaust air muffler can be considered as a unification configuration.

[0032] And H2 NOX to depend NOX which returns In a purge, it can consider as the configuration which installed the soot trapper and the unburnt glow product oxidation means in the upstream of a reforming catalytic converter as an object for Diesel engines. Moreover, in this example, a hydrogen fueled engine besides a gasoline engine and a diesel power plant is satisfactory for an internal combustion engine, and they are these NOX(s). It can apply effective in reduction equipment. In the case of this hydrogen fueled engine, a hydrogen generator is not required and it is H2 as a fuel. It is applicable by supplying in bypass through a controller.

[0033]

[The 1st example] The 1st example which applies the system of this invention to the lean burn engine of an engine displacement 11 is shown in drawing 6 . engine E1 of the 1st example Engine E1 with which lambda=0.8-1.0 (rich side) and service conditions other than this operate by the rarefaction side of lambda=1.2-1.8 at the time of the full load of the excess air factor lambda= 0.95 at the time of an idle - 1.0 (they are rich side or theoretical air fuel ratio a little than theoretical air fuel ratio) each rotational frequency, and rapid acceleration it is . Therefore, O2 under exhaust air It changes to about 0 - 10%. Exhaust system Ex It is the configuration which installs an oxidation catalyst 9 in the outlet of an exhaust manifold 8, oxidizes and purifies incomplete combustion products, such as HC and CO. Furthermore, a reduction catalyst 12 is arranged to the downstream of the muffler 13 as a silencer. In the inlet port of a reduction catalyst 12, it is H2. The mixer 10 is formed in order to equalize mixing with exhaust air.

[0034] H2 A generator 11 is the water electrolysis H2 using the reforming catalyst 14 as shown in drawing 7 and drawing 8 . It is a generator.

[0035] the electromagnetism which the hydrogen generator 11 forms a coiled form inner core in the branched exhaust pipe, and injects a methanol at the end of an inner core -- the fuel injection valve is prepared and the other end is led to the mixer. It is filled up with the porous ceramic for near the inlet port of an inner core to evaporate a methanol, and the reforming catalyst of a pellet type is got blocked in after that. (When using a monolith-like catalyst, an inner core is changed in the shape of a straight line from a coiled form.) The catalyst is using Pd. The inside of drawing 6 and 15 are an engine E1. It is the inhalation air content sensor which measures an air content, and 16 is NOX under exhaust air. NOX which measures concentration It is a sensor.

[0036] In the case of **** 1 example, it is NOX. It is H2 of the equivalent at a mol. Since it needs, it is an engine E1. NOX under exhaust air Although based also on concentration, at the H2 of 0.3 l/min, and maximum output maximum horsepower hour, it is H2 of 1.0 l/min extent at the time of the vehicle speed of 50km/h. It needs. This H2 Consumption H2 under each service condition although some fuels are reformed and it is supplied The effect affect transit fuel consumption is 1 - 2% or less, is extent which can be disregarded if compared with 15 - 20% of fuel consumption reduction merits using a lean burn engine, and does not spoil the low-fuel-consumption property of a lean burn engine.

[0037] Moreover, H2 The methanol which generating takes is 0.15 l/min (steam) extent to 50 km/h transit.

[0038] **** 1 example is a little fuel as mentioned above H2 It reforms in a generator 11, the low temperature side property of a reduction catalyst 12 is used, and it is H2-NOX. Since it returns, it is an engine E1. It is NOX regardless of the operation excess air factor lambda. Practically significant lean burn NOX which can measure reduction It is a reduction system. Moreover, H2 CO which carries out a byproduction is a water gas shift reaction [0039].

[Formula 5]

$$CO + H_2O \rightarrow H_2 + CO_2$$

[0040] It comes out and is H2. It changes or is H2 by Pd film. It separates into CO and is high grade H2. There is also the approach of carrying out and supplying ahead of a reduction catalyst 12. However, CO which carries out a byproduction is a minute amount, can be committed in a reduction catalyst 12 as a reducing agent as it is, and does not emit CO.

[0041]

[The 2nd example] The 2nd example is the case of the gas engine used for the object for air-conditioning, and a generation of electrical energy. A fuel shows the case of natural gas. Unlike the object for automobiles, the engine for stationing of such a purpose is operated by the fixed rotational frequency and the fixed load. Therefore, it is easy to keep the temperature of a reforming catalytic converter constant. Since the configuration of the 2nd example is almost the same as that of said 1st example as shown in drawing 9 , the same part attaches the same agreement and omits explanation.

[0042] Unlike the 1st example, the fuel supplied to a hydrogen generator is required H2 which is natural gas, mixes with air and is supplied. In order to secure, air and natural gas are controlled by the regulator valve. Control is the same as that of said 1st example almost, and does so the almost same operation effectiveness as said 1st example.

[0043]

[The 3rd example] Some fuels are reformed in said each example, and it is H2. They are combination and NOX about the equipment and the zeolitic catalyst which make it generate. NOX of the engine which carries out reduction purification Reduction equipment is H2. It is NOX by conditions of supply and the contents. It has turned out that a big difference is produced for the reduction engine performance. As shown in drawing 10 , it is NOX and O2. It is exhaust air of the included engine from the upstream of a sink and a reforming catalytic converter to a catalyst H2 NOX at the time of supplying The rate of purification is shown in drawing 11 . Setting to drawing 11 , an axis of abscissa is NOX. H2 receiving A supply rate is shown and 1.0 is NOX. H2 It is the case where it is the equivalent. An axis of ordinate is NOX by reduction. It is the rate purified and 1.0 is NOX. It is shown that all will be purified.

[0044] When the catalyst 61 of the pellet type shown in drawing 12 is contained in the reforming catalytic converter 60 shown in drawing 10 , the high rate of purification is shown that drawing 14 shows. When it is made the catalyst 62 of a monolith type shown in drawing 13 , it is the H2 [same]. Even if it is the amount of supply, the rate of purification falls.

[0045] The catalyst 61 of the pellet type shown in drawing 12 is H2 in an inlet port. Exhaust gas is not mixed enough but it is H2. Even if there is concentration distribution, the clearance between pellets like a maze is enough mixed in the process in which gas is in direct communication and goes, and it is H2. Exhaust gas is equalized.

[0046] On the other hand, since the cross-section "swage block"-like hole is ********(ed) and the hole of a piece has been independent to the gas flow direction, the catalyst 62 of a monolith type shown in drawing 13 is H2 in an inlet port. If there is distribution, it will be hard to mix the gas in the passage which adjoins each other mutually on the way. It is difficult to make the size of an exhaust pipe thick sharply from the constraint on mount according to the actual experiment, a gas flow rate is quick, and it is H2. A high concentration field is made near a center section, and it is H2 in a monolith periphery. It has produced un-arranging [which is hardly supplied]. Therefore, a monolith type is H2. A utilization factor is low compared with a pellet type.

[0047] On the other hand, when it sees as an engine pumping system, a pellet's rubbing mutually and tending to carry out disintegration by vibration, and the direct cross-sectional area of gas of a pellet type are small, and its passage resistance is strong, it causes exhaust-gas-pressure increase, and has the fault which gets worse in the engine performance itself. Therefore, although it is desirable to use a monolith type for a catalyst, it is H2 in this case. A device is needed for supply.

[0048] Then, the 3rd example is NOX which was superior to the pellet type using the catalyst of a monolith type. It is H2 so that the rate of purification may be obtained. It consists of simple equipment on the configuration which carries out homogeneity mixing of the supply. Namely, H2

as mixed equipment 69 The fundamental structure of the jet nozzle 63 is shown in drawing 14 and drawing 15 . Inserted H2 jet nozzle 63 is a hollow cylinder configuration, and it has turned at it in the shape of L character to the flow direction of exhaust air, and it has two or more jet holes 64 in a radial. 4-6 pieces are suitable and the jet hole 64 of a radial is one train or two or more successive installation eclipse ******. (Three trains of jet holes are arranged in drawing 14).
[0049] Since resistance of passage will become large if D is required for d 20% or more and d is enlarged, the insertion tube outer diameter d of the jet nozzle 63 and the bore D of an exhaust pipe 65 carry out cross-section expansion formation of some exhaust pipes 65, as shown in drawing 16 . Moreover, even if the distance L from the jet nozzle 63 to the reforming catalytic converter 60 needs the more than twice [at least] of D and enlarges them 10 or more times, an improvement effect has it. [little] Mixed equipment can show the configuration other than a **** to drawing 17 and drawing 18 . H2 [namely,] the part made to stir -- H2 of a minor diameter it consists of the cylinder like object with base 68 which formed two or more jet holes 67 by the major diameter from the jet nozzle 66 and this at a wall -- about two-fold are constituted tubular. H2 spouted It is H2 first. It mixes with the exhaust air which flows into the jet nozzle 66 with the dynamic pressure of exhaust gas pressure, and it blows off from the container liner of a cylinder like object with base 68 in an outer case, and between inside-and-outside cylinders is further mixed with the flowing exhaust air. Thus, since it passes through two steps of mixing processes, H2 and exhaust air can carry out homogeneity mixing completely mostly.
[0050] The magnitude (a diameter or cross section) of an inside-and-outside cylinder influences mixing greatly, and if a container liner is small, almost all exhaust air flows an outer case, and it cannot use dynamic pressure enough. In drawing 17 and drawing 18 , as for D/d (an outer case/container liner), three to about 1.7 are [the diameter ratio of an inside-and-outside cylinder] effective, and the two neighborhoods are best.
[0051] Mixing becomes good, and even if the 3rd example which consists of the above-mentioned configuration is a monolith type, it can obtain the same rate of purification as a pellet type. It sets to the rate of the same purification, and is supply H2. Since an amount can be saved 30 to 60%, the fuel which H2 generating takes can be lessened and an engine output and the effect on fuel consumption can be mitigated.
[0052] For example, if the usual operation region representation point estimates in a 1.6l. lean burn gasoline engine, they are engine-speed 2000rpm and torque 40Nm and NOX at this time. Burst size 0.44 l/min and this NOX H2 H2 taken to purify by reduction A flow rate is 0.66 l/min. H2 of 0.66 l/min It is H2 to making it generate. The fuel for a generator becomes fuel vapor of 0.33 l/min (in the case of a methanol).
[0053] It will be H2 if drawing 17 which is D/d=2, and the equipment shown in drawing 18 perform mixed promotion. The amount of supply is NOX. It ends with equivalent 0.44 l/min extent, and a fuel falls to the steam of steamy 0.22 l/min of 0.22 l/min. That is, it becomes saving of 0.11 l/min.
[0054]
[The 4th example] In said example, hydrogen is generated by the hydrogen generator using a zeolitic catalyst, and it is H2. NOX supply the inlet port of a zeolitic catalyst and according to H2 If it returns, it will be O2 of high concentration [under / exhaust air]. It is big NOX even if it exists. The rate of purification is obtained.
[0055] However, the conventional NOX Compared with a catalyst, for example, a three way component catalyst, and Cu-zeolitic catalyst, it is a low-temperature reaction, and SV (for example, 10,000-60,000) small from the relation of a reaction rate must be used compared with the conventional catalyst using the SV values (ratio of passage quantity-of-gas-flow l/hr and the catalyst volume l) 50,000-100,000. When mounting this system, the reforming catalytic converter of this system consists of inlet gas temperature, a lower stream of a river, for example, near an exhaust air muffler, an exhaust system. however, it is the location in which a reforming catalytic converter with a large (the magnitude of a converter -- large) car structure top SV value is installed in a car, and is hard to apply to all cars.

[0056] **** 4 example is Lean NOX in order to make installation of a reforming catalytic converter easy. Even if it makes a catalyst build in the muffler structure and the muffler for making a catalyst build in a muffler and measuring miniaturization, it is temperature conditions to NOX. Purification is made possible.
[0057] That is, the configuration of the 4th example is Lean NOX to the exhaust air muffler 80, as shown in drawing 20 and drawing 21 . It is NOX if a catalyst 82 is made to build in. A converter and since it ends with one of the two, without arranging an exhaust air muffler to a serial, it becomes very [in arrangement tooth space] advantageous. The reforming catalytic converter 83 which gave the silencing effect which built the monolithic catalyst 82 (Pt-zeolite system) in the exhaust air muffler 80 to drawing 20 and drawing 21 is shown.
[0058] It is H2 from the upstream of the reforming catalytic converter 83. The exhaust air by which mixing mixing was carried out flows from the direction of an arrow head, it collides with the mixing plate 84, the circulation hole 85 of size plurality of this mixing plate 84 is passed, and it is exhaust air and H2. It flows into a monolithic catalyst 82, mixing enough. Since the circulation hole 85 is not formed in the core which becomes the exhaust air rate-of-flow max on the mixing plate 84, it is H2. It does not concentrate on a monolith core. the circulation hole 85 of the mixing plate 84 -- each size -- it differs in a diameter, and since two or more arrays are carried out, while the passage rates of flow differ and stirring of gas takes place, a silencing effect is done so by interference.
[0059] By the way, as for an exhaust air muffler, it is common to be arranged in the tail end of an engine exhaust system, and since it is cooled on the way, the inlet gas temperature of an exhaust air muffler becomes low. Even the maximum-engine-speed maximum horsepower hour of an engine with the highest inlet temperature is 150-200 degrees C, and is about 100-150 degrees C in a service condition with usually high operating frequency.
[0060] The conventional three way component catalyst and Lean NOX of Cu-zeolite system Since sufficient reaction is not expectable unless it is 300-400 degrees C or more, a catalyst cannot be made to build in in a muffler with a catalyst. It sets in said example and is H2. When performing reduction to depend, it was shown that it can purify at low temperature, but temperature is about 150-300 degrees C, and if compared with the inlet temperature of an exhaust air muffler, it is in a little high temperature requirement.
[0061] this invention person etc. is O2. It is H2 under coexistence. NOX to supply It examined [various] experimentally what should be selected as a catalyst component about the activity of a reduction catalyst. Consequently, Pd and Rh did not have activity, activity of Cu was bad and Pt found out that high activity was shown. However, Pt needs to be high distribution and support, such as an alumina which has high specific surface area (more than at least 100m2 / g) for that purpose, a silica, and a zeolite, is required for it.
[0062] furthermore, this invention person etc. -- NOX Lean NOX of reduction A catalyst and H2 Pretreatment which should be performed before mixing was considered by boiling many things. The result is shown in drawing 19 . It is H2 to engine exhaust air. It mixes and is NOX. Lean NOX of reduction When it leads to a catalyst (Pt system), as shown in Curve B, the apex of activity is near 250 degree C among drawing 19 .
[0063] It is H2, after establishing an afterburner, a reactor, a three way component catalyst, an oxidation catalyst, etc. near an engine manifold, oxidizing CO and HC and carrying out reduction removal beforehand. It supplies and is NOX. When led to the reforming catalytic converter of reduction, as shown in the curve A in drawing 19 , activity temperature shifted to the low temperature side, and it newly found out that high activity was shown at 100-150 degrees C.
[0064] In accordance with the inlet temperature of an exhaust air muffler, this temperature was closed, if [for the first time] by building in the reduction catalyst 80 of Pt-zeolite system in the exhaust air muffler 80. Furthermore, he is Lean NOX after removing HC and CO. NOX by the catalyst The direction which purified can also improve the rate of purification and it is HC-O2. The practically excellent operation effectiveness which does not form soot on a catalyst from an imperfect reaction is done so.
[0065] Furthermore, it is the interference tube Ex1 after a monolithic catalyst 82. The silencing effect is made more into fitness by installing. Drawing 22 does so the same operation

effectiveness as drawing 20 and drawing 21 , and differs in the gestalt of the mixer section with said mixing plate, and the points used as the mixing pipe 86 which is hollow tubed part material differ. The 4th example which consists of the above-mentioned configuration is NOX high at all operating ranges while doing so the practical effectiveness that become compact and mount nature becomes good, since the reforming catalytic converter 83 and the exhaust air muffler 80 can consider as a unification configuration. The outstanding effectiveness which can maintain the rate of purification is done so.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The block diagram showing the basic configuration of the example of this invention
[Drawing 2] The diagram showing an air-fuel ratio and the relation of a fuel economy
[Drawing 3] Fuel consumption and NOX of a lean burn engine Diagram showing relation
[Drawing 4] Lean NOX Diagram showing the property of a catalyst
[Drawing 5] H2 The rate of supply, and NOX Diagram showing the relation of the rate of purification
[Drawing 6] The block diagram showing the outline of the 1st example equipment of this invention
[Drawing 7] H2 in the 1st example equipment Sectional view of a generator
[Drawing 8] H2 of others in the 1st example equipment Block diagram expanding and showing the important section of a generator
[Drawing 9] The block diagram showing the outline of the 2nd example equipment of this invention
[Drawing 10] The block diagram showing the outline of the 3rd example equipment of this invention
[Drawing 11] It is related with the 3rd example equipment and is NOX. Diagram showing the relation of the rate of purification
[Drawing 12] The schematic diagram showing a pellet type catalyst configuration about the 3rd example equipment
[Drawing 13] The schematic diagram showing the catalyst configuration of a monolith type about the 3rd example equipment
[Drawing 14] Drawing of longitudinal section showing the outline of the 3rd example equipment of this invention
[Drawing 15] The cross-sectional view showing the outline of the 3rd example equipment of this invention
[Drawing 16] The schematic diagram showing the outline of the 3rd example equipment of this invention
[Drawing 17] Drawing of longitudinal section showing the example of others of the 3rd example equipment of this invention
[Drawing 18] The cross-sectional view showing the example of others of the 3rd example equipment of this invention
[Drawing 19] It is related with the 4th example of this invention, and is NOX. Diagram showing the rate situation of purification
[Drawing 20] Drawing of longitudinal section showing the outline of the 4th example equipment of this invention
[Drawing 21] The cross-sectional view showing the outline of the 4th example equipment of this invention
[Drawing 22] Drawing of longitudinal section showing the configuration of others of the 4th example equipment of this invention
[Description of Notations]

E, E1 Engine
1 11 H2 Generator
3, 13, 80 Silencer
12 60 Reduction catalyst
9 Oxidation Catalyst
5 Inhalation Air Content Sensor
6 NOX Sensor
7 Control Power Source
10 Mixer

[Translation done.]

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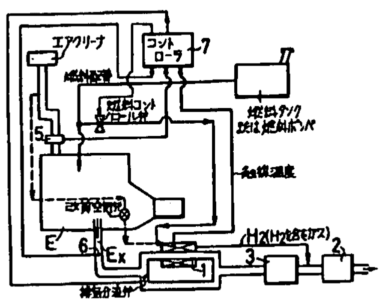
最終頁に続く

(54)【発明の名称】　内燃機関の窒素酸化物低減装置

(57)【要約】
【目的】　リーンバーンエンジンやディーゼルエンジン等において当該エンジンの燃費の良さを損なうことなく排気ガス中のO_2の濃度如何を問わずNO_xを有効に還元浄化し得る内燃機関のNO_x低減装置を提供する。
【構成】　内燃機関Eの燃焼室で供給燃料の燃焼による排気中にNO_xとO_2の存在のもと、排気系統Exに設けH_2とNO_xを接触反応しNO_xを浄化する触媒装置2の入口側に、メタノール又はLPG、天然ガス等の炭化水素燃料の一部を改質触媒コンバータによってH_2を生成する水素発生装置1からのH_2を供給し、排気系統の消音装置付近における排気低温雰囲気下で該H_2により前記排気中のNO_xを直接還元浄化して該NO_xを効率良く低減する。



【特許請求の範囲】
【請求項1】　内燃機関の燃焼室で燃料供給装置より供給された燃料の燃焼による排気中に窒素酸化物と酸素ガスの存在のもと、排気系統内で水素ガスと窒素酸化物を触媒反応させ、窒素ガスと水に分解するための触媒装置を設けると共に、該触媒装置の入口側にメタノール又はLPG、天然ガスなどの炭化水素燃料の一部を改質触媒コンバータによって水素を生成する水素発生装置を設け、水素ガスを供給可能に構成し、排気系統の消音装置付近における排気低温雰囲気下で該水素発生装置からの水素ガスにより前記排気中の窒素酸化物を直接還元浄化して該窒素酸化物を低減するようにしたことを特徴とする内燃機関の窒素酸化物低減装置。

【発明の詳細な説明】
【0001】
【産業上の利用分野】本発明は、内燃機関の窒素酸化物低減装置に係り、特に、希薄混合気を使用し、燃料消費向上をめざす、いわゆるリーンバーンエンジンやディーゼルエンジン、その他の水素エンジン等において、当該エンジンの燃費の良さを損なうことなく、排気中の酸素ガス（以下O_2と称す）の濃度如何を問わず窒素酸化物（以下NO_xと称す）を有効に還元浄化しうるリーンNO_x触媒排気浄化システムに関する。
【0002】
【従来の技術】内燃機関、主としてピストン機関において排気の窒素酸化物（以下NO_xと称す）の低減方法には、従来、
① 三元触媒によるNO_x低減法
② 超希薄空燃比の利用
③ リーンNO_x触媒によるNO_x低減法（例えば、特開平1－139145号公報）
の三つが考えられている。しかしながら、①の方法はエンジンに供給される燃料と空気の重量比が約14．5、即ち理論空燃比でなければならない。もし理論空燃比より燃料が希薄な空燃比を使用するとNO_xは低減しない。しかるに燃料消費の経済性を考えると図2に示すように理論空燃比より希薄側でエンジンを運転した方が燃料消費率が少なく、効率が良いことが知られている。
【0003】次に②はいわゆるリーンバーンエンジンによってNO_x低減と燃費低減を両立させようとするものである。しかし、NO_xを十分低減できる空燃比を使おうとすれば、燃焼の失火限界に近づき、エンジンの燃費が悪くなるばかりでなく、運転が荒れ、ドライバビリティも悪くなる。これを防止するためシリンダ内の空気流れに乱れや流速増加を計り、燃焼速度を速くして失火限界をより希薄域になるように改良しようとするものがある。しかし、空気乱れや流速増加を過度に行うと、かえって着火時の火炎核形成や燃焼初期の火炎伝播が妨げられるため、この方法による失火限界の拡大には限界がある。また、シリンダ内の空燃比分布を調整して点火栓近傍のみ着火に適した濃混合気とする方法もあるが、図3に示すように失火限界がより希薄側に移ると、発生NO_xも破線で示したように、減少する割合が少なくなるので大きな効果は期待できない。
【0004】③は上記②の欠点を補うため、失火限界よりやや理論空燃比に近い燃料消費率最低点付近を使って運転し、やや低減不足のNO_xはゼオライト系リーンNO_x触媒で浄化しようとするものである。この方法は燃費の良いシステムになる可能性がある。しかしながら、このリーンNO_x触媒は、排気中に大量のO_2存在下でNO_xを還元することになり、温度条件などが厳しく、現状では充分な触媒のNO_x浄化率と耐久性が両立しにくいといった実用上解決すべき問題がある。以上のようにエンジンの燃料消費率を極力小さくできる空燃比を使いながらNO_xを充分低減する方法にはいずれも実用上の問題が多い。
【0005】ところでリーンバーンエンジンでもディーゼルエンジンでも排気中に過剰O_2を含むことは基本的に同じであるが、このエンジンの排気は、排気中にO_2を含み、希薄混合気を使うほどO_2濃度は大きくなる。このようなO_2を含む排気中のNO_x還元浄化を行う触媒をリーンNO_x触媒といい、貴金属系、例えばゼオライト系の触媒が使われることが多い。このリーンNO_x触媒では、NO_x浄化率と温度との関係が図4に示すようになっている。そして、350℃以上の高温域は、主としてHC－NO_xの反応である。250～350℃以下の低温域は、NO_xのH_2による還元反応となり、NO_xの浄化が可能である。
【0006】しかし、リーンNO_x触媒は、エンジンの排気マニホールド付近に設置されるので、排気温度が最高800～900℃にも達し、かつリーンバーンエンジンの排気は空燃比が理論空燃比より希薄側を使うので、排気中にH_2は殆ど存在しない。従って、従来、低温側の特性は、利用不可能な領域であった。
【0007】
【発明が解決しようとする課題】本発明の目的は、上記従来の種々の問題を解決するもので、リーンバーンエンジン又は常にO_2（空気）過剰側で運転されるディーゼルエンジンの排気中にNO_xとO_2の共存のもとでリーンバーンエンジンまたはディーゼルエンジンの燃費の良さを損なうことなく、排気中のO_2の濃度如何を問わずNO_xを有効に還元浄化する排気浄化システムすなわち、NO_xの放出量を抑制し得る内燃機関のNO_x低減装置を提供しようとするものである。
【0008】
【課題を解決するための手段】本発明の内燃機関のNO_x低減装置は、内燃機関の燃焼室で燃料供給装置より供給された燃料の燃焼による排気中にNO_xとO_2の存在のもと、排気系統内でH_2とNO_xを触媒反応させNO_xを浄化するための触媒装置を設けると共に、該触媒装

置の入口側にメタノール又はＬＰＧ、天然ガス等の炭化水素燃料の一部を改質触媒コンバータによって水素を発生する水素発生装置を設けてH_2を供給可能に構成し、排気系統の消音装置付近における排気低温雰囲気下で該水素発生装置からのH_2により前記排気中のNO_xを直接還元浄化して該NO_xを低減するようにした構成である。

【0009】

【作用効果】上記構成からなる本発明の内燃機関のNO_x低減装置は、以下の作用を奏する。

【0010】すなわち、本発明者等が案出した本発明の内燃機関のNO_x低減装置は、図１に示すような構成とすることによって、内燃機関の燃焼室で供給燃料の燃焼による排気中にNO_xとO_2の存在のもと、H_2とNO_xを接触反応させ、窒素ガスと水に分解する排気系統に設けた触媒装置の入口側にメタノール又はＬＰＧ、天然ガスなどの炭化水素燃料の一部を改質触媒コンバータに導きH_2を生成する水素発生装置からのH_2を供給し、排気系統の消音装置付近における排気低温雰囲気下で該H_2により前記排気中のNO_xを効率良く的確に直接還元浄化して該NO_xを低減する作用効果を奏する。このため、本発明の内燃機関のNO_x低減装置は、エンジンの使用空燃比が理論空燃比より過濃側、理論空燃比、理論空燃比より希薄側と排気中のO_2の存在又はO_2の濃度に関係なくNO_xを触媒によって低減できるのでエンジン（自動車）性能上、燃費上NO_x低減条件を考慮せずに最適値を選ぶことができる有利さを持たせ得る。

【0011】

【実施例】実施例における水素発生装置はエンジンに使用する燃料によって改質触媒コンバータが次のように分類される。

【0012】すなわち、メタノールを燃料とするエンジンにあっては

１）Pd、Pt、Cu／Cr／Ni等の遷移金属触媒を用い、メタノールを排気によって加熱蒸発させたガスを、この触媒に導きH_2を生成する。触媒入口ガス温度は３００℃程度が最良であって、この時の反応は

【0013】

【化１】

$$CH_3OH \rightarrow CO + 2H_2$$

【0014】となる。

【0015】２）メタノール蒸気に空気を混合させ、Cu−Ni−Cr／アルミナ触媒によってメタノールの一部を部分酸化させ、H_2を生成する。温度は４００℃〜５００℃が適当であり、メタノールに混入させる空気流量をコントロールし、温度を保つようにする。この場合の反応は、

【0016】

【化２】

$$CH_3OH + Air \rightarrow H_2 + CO + H_2O$$

【0017】となる。

【0018】３）触媒にCu−MnまたはCu−Znを用い、メタノールに水蒸気を加えるかまたは空気やメタノール水を加え水蒸気改質を行う。温度は２５０℃程度が適当で、反応は

【0019】

【化３】

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

【0020】となる。

【0021】また、ＬＰＧ、天然ガスなどの炭化水素燃料を使うエンジンにあっては、触媒としてNi、Co、Rhを使い、温度３００〜８００℃で改質する。この炭化水素燃料の場合には、水蒸気や空気や水タンクからの水を加えて改質を行う。（触媒により温度が異なる。低温ではメタンが多く、高温ではCOが多い）。反応としては、

【0022】

【化４】

$$HC + H_2O \rightarrow H_2 + CH_4 + CO_2 \quad 300\sim500℃$$

$$HC + H_2O \rightarrow H_2 + CO + CO_2 \quad 800℃$$

$$HC + Air \rightarrow H_2 + CO \quad 800℃$$

$$HC + 排気 \rightarrow H_2 + CO \quad 700℃$$

（ＥＧＲ改質）

【0023】となる。

【0024】また、本実施例の内燃機関のNO_x低減装置は、前記排気系統の排気管に装備するNO_xセンサ６と吸入空気量センサ５の出力からNO_x流量を算出し、常に適正なH_2量を決定し前記水素発生装置としての改質触媒コンバータを加熱するエンジン排気流量又は部分酸化を行う場合の空気量および改質燃料量を制御する構成とすることもできる。

【0025】さらに、本実施例の内燃機関のNO_x低減装置は、当該内燃機関の回転数、吸気管負圧、吸気絞り弁開度又は燃料供給装置としての噴射ポンプの噴射量等の内燃機関における運転条件を検知できるセンサを具備し当該センサの出力からNO_x流量を予測演算し前記水素発生装置の改質触媒コンバータに供給する燃料量をコントロールする学習制御方式にした構成とすることもできる。

【0026】しかも、本実施例の内燃機関のNO_x低減装置は、前記触媒装置の入口側においてH_2と排気の混合を均一にするため、ミキサーを具備したり、または、排気系統の消音装置を有効利用する構成とすることもできる。

【0027】詳述すれば、本実施例の内燃機関のNO_x低減装置は、前記従来の問題を解消するために案出されたものでその基本構成図を図１に示す。すなわち、本実施例の第１のポイントは、このH_2還元が排気低温側でエンジンＥの全運転範囲において使用することである。第２のポイントは、低温側の利用を可能にするため構成システム中にH_2発生器１を組み込むことである。第３のポイントは、エンジンＥの運転状態又は排気中のNO_x量によってH_2発生器１を制御し、常に排気中NO_xとモルで当量程度又は過剰のH_2が供給できるようにすることである。

【0028】還元触媒２は高温にさらされるとH_2がO_2と反応しH_2-NO_xの選択性が失われるので、３５０℃以上にさらされることのないよう消音器３の付近に配置する。そして、本実施例は、燃料配管から分岐し、流量コントロール弁を介してH_2発生器としての改質触媒コンバータに燃料を導入改質してH_2を発生させる。H_2は、還元触媒２の入口付近に供給する。供給するH_2は、排気中のNO_xとモルで当量程度にするためにエンジンＥの吸入空気量センサ５によって空気量を測定し、排気中のNO_x濃度をNO_xセンサ６によってを求め、コントローラ７で両センサ５、６の出力からNO_x流量を演算した上で、NO_x流量に対応するH_2を発生させるため改質触媒コンバータに導入する燃料流量や、排気分流弁による改質触媒コンバータ温度、部分酸化を行うものでは改質用空気弁の制御を行う構成である。

【0029】図５において、横軸は、NO_xに対するH_2の供給比、縦軸は、NO_xの還元率（浄化率）を示す。NO_xに対して等量の（モル）H_2を供給すれば、もしNO_xとH_2が完全に混合するものとすればNO_xはすべて還元浄化される（理論値）。しかし実際には完全混合されないので還元率は実験値のようになる。理論より実験値の方が浄化率が良くなっている部分があるが、これは排気中の水蒸気が貴金属系触媒上で分解しH_2に変換していることによる。従って、供給したH_2より多くのH_2がNO_xと反応する。

【0030】その他の実施例としては、H_2による還元浄化を行うNO_x低減装置において改質触媒コンバータの入口側にH_2と排気とを混合ミキシングするミキサーを設置する機能とすることができる。また本実施例のその他のNO_x浄化装置である水素発生器および触媒装置は、それぞれ好適な作動温度範囲を持つため、内燃機関の排気系統において水素発生器を排気マニホールドの出口に設置した酸化触媒の後段に、また還元触媒は排気が膨張し温度が２００℃以下に下がるマフラー内、あるいはその下流に設置することができる。

【0031】さらに、その他の実施例としては、水素発生器のH_2を供給してO_2共存下のエンジン排気中のNO_xを還元浄化するNO_x低減装置において、エンジンの排気マニホールド付近に酸化触媒、三元触媒、排気リアクタ等のHC、COを酸化する手段を持ち、かつリーンNO_x触媒としての改質触媒コンバータにPt−ゼオライト系触媒を用いる構成とすることができる。また、改質触媒コンバータに消音効果を持たせ改質触媒コンバータと排気マフラーを一体化構成とすることができる。

【0032】しかも、H_2によるNO_x還元を行うNO_x浄化装置において、ディーゼル機関用として改質触媒コンバータの上流にスートトラップ、未燃焼生成物酸化手段を設置した構成とすることができる。また、本実施例において、内燃機関はガソリンエンジン、ディーゼルエンジンの他、水素エンジンでも良く、これらのNO_x低減装置に有効に適用し得る。この水素エンジンの場合は、水素発生装置が必要でなく、燃料としてのH_2をコントローラを介してバイパス的に供給することにより適用することができる。

【0033】

【第１実施例】エンジン排気量１１のリーンバーンエンジンに本発明のシステムを適用する第１実施例を図６に示す。第１実施例のエンジンE_1は、アイドル時の空気過剰率λ＝０．９５〜１．０（理論空燃比よりやや過濃側か理論空燃比）各回転数の全負荷時および急激加速時はλ＝０．８〜１．０（過濃側）、これ以外の運転条件はλ＝１．２〜１．８の希薄側で運転するエンジンE_1である。従って、排気中のO_2は、０〜１０％程度まで変化する。排気系統E_1は、排気マニホールド８の出口に酸化触媒９を設置し、HC、CO等の不完全燃焼生成物を酸化し浄化する構成である。さらに、消音器としてのマフラー１３の下流側に還元触媒１２を配置する。還元触媒１２の入口にはH_2と排気との混合を均一化するためミキサー１０が設けられている。

【0034】H_2発生器１１は、図７、図８に示すように改質触媒１４を用いた水電解H_2発生器である。

【0035】水素発生器１１は分岐された排気管内にコイル状のインナーコアを形成し、インナーコアの一端にはメタノールを噴射する電磁燃料噴射弁が設けてあり、他端はミキサーに導かれている。インナーコアの入口付近はメタノールを蒸発させるための多孔セラミックが充填してあり、その後にはペレット状の改質触媒が詰まっている。（モノリス状の触媒を使うときはインナーコアをコイル状から直線状に変更する。）触媒はPdを使っている。図６中、１５はエンジンE_1への空気量を測定

する吸入空気量センサで、16は排気中のNO_x濃度を測定するNO_xセンサである。

【0036】本第1実施例の場合、NO_xとモルで当量のH_2を必要とするので、エンジンE_1の排気中のNO_x濃度にもよるが、50km／hの車速のとき0.31／minのH_2、最大出力最大馬力時では1.01／min程度のH_2を必要とする。このH_2は燃料の一部を改質して供給されるものであるが、それぞれの運転条件下における消費H_2が走行燃費に及ぼす影響は1～2％以下であり、リーンバーンエンジンを使う燃費低減メリット15～20％に比べれば無視できる程度であり、リーンバーンエンジンの低燃費特性を損なうことがない。

【0037】また、H_2発生に要するメタノールは、50km／h走行で0.151／min（蒸気）程度である。

【0038】以上のように本第1実施例は、少量の燃料をH_2発生器11において改質して還元触媒12の低温側特性を利用して、H_2－NO_x還元を行うので、エンジンE_1の運転空気過剰率λに無関係にNO_xの低減が計れる実用上有意義なリーンバーンNO_x低減システムである。また、H_2と共に副生するCOはシフト反応

【0039】

【化5】

$$CO + H_2O \rightarrow H_2 + CO_2$$

【0040】でH_2に変換するか、またはPd膜によりH_2とCOとに分離し、高純度なH_2として還元触媒12の前方に供給する方法もある。しかし、副生するCOは微量であり、そのまま還元剤として還元触媒12の中で働くことができ、COを放出することはない。

【0041】

【第2実施例】第2実施例は、空調用、発電用等に使うガスエンジンの場合である。燃料は天然ガスの場合を示す。このような目的の定置用エンジンは自動車用と異なり、一定回転数、一定負荷で運転される。従って、改質触媒コンバータの温度は一定に保ち易い。第2実施例の構成は図9に示すように前記第1実施例とほぼ同一であるので、同一部分は同一符合を付して説明を省略する。

【0042】水素発生器に供給する燃料は第1実施例と異なり、天然ガスであり、空気と混合して供給する必要なH_2を確保するため、空気、天然ガスとも調整弁によってコントロールする。コントロールは、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同様の作用効果を奏する。

【0043】

【第3実施例】前記各実施例において、燃料の一部を改質してH_2を発生させる装置とゼオライト系触媒を組合せ、NO_xを還元浄化するエンジンのNO_x低減装置は、H_2の供給条件、内容によってNO_x低減性能に大きな差異を生じることが分かってきた。図10に示すように、NO_x、O_2を含むエンジンの排気を触媒に流し、改質触媒コンバータの上流からH_2を供給した場合のNO_x浄化率を図11に示す。図11において横軸はNO_xに対するH_2の供給割合を示し、1.0は、NO_xとH_2が当量の場合である。縦軸は還元によってNO_xが浄化される割合であって、1.0はNO_xがすべて浄化されてしまうことを示す。

【0044】図10に示す改質触媒コンバータ60内に、図12に示すペレットタイプの触媒61が入っている場合は図14から分かるように高い浄化率を示す。図13に示したモノリスタイプの触媒62にすると、同じH_2供給量であっても浄化率は低下する。

【0045】図12に示したペレットタイプの触媒61は、入口でH_2と排気ガスとが十分混合せず、H_2に濃度分布があっても迷路のようなペレットの隙間をガスが直進して行く過程で十分混合し、H_2と排気ガスが均一化される。

【0046】一方、図13に示したモノリスタイプの触媒62は、断面"蜂の巣"状の孔をが多数有しており、一個の孔はガス流れの方向に独立しているので、入口でH_2に分布があれば途中で互いに隣り合う流路内のガスが混合しにくい。実際の実験によれば、排気管の太さは車載上の制約から大幅に太くすることは困難でガス流速は速く、H_2は中央部付近に高濃度領域を作り、モノリス周辺部にはH_2がほとんど供給されない不都合を生じている。従って、モノリスタイプは、H_2の利用率がペレットタイプに比べ低い。

【0047】一方、エンジン排気システムとして見ると、ペレットタイプは振動によってペレットが互いに擦れ合って粉末化し易いこと、ガスの直通断面積が小さく、通過抵抗が大きく、排圧増大を招き、エンジン性能自身を悪化する欠点がある。従って、触媒にはモノリスタイプを使うことが望ましいが、この場合にはH_2の供給に工夫が必要になる。

【0048】そこで、第3実施例は、モノリスタイプの触媒を使いペレットタイプより優れたNO_x浄化率を得るようH_2の供給を均一混合する構成上簡素な装置から成る。すなわち、混合装置69としてのH_2噴出ノズル63の基本的構造を図14、図15に示す。挿入されたH_2噴出ノズル63は、中空円筒形状で、排気の流れ方向にL字状に曲がっており、放射状に複数の噴出孔64を有する。放射状の噴出孔64は、4～6個が適当で、1列又は複数列設けられている。（図14では噴出孔が3列配設されている）。

【0049】噴出ノズル63の挿入管外径dと排気管65の内径DとはdがDの20％以上必要で、dを大きくすると流路の抵抗が大きくなるので図16に示すように排気管65の一部を断面拡大形成する。又、噴出ノズル63から改質触媒コンバータ60までの距離LはDの少なくとも2倍以上を必要とし、10倍以上大きくしても改善効果は少ない。混合装置は、上述の他に、構成を図17、図18に示すようにすることができる。すなわち、H_2を攪拌させる部分は、小径のH_2噴出ノズル66とこれより大径で壁部に複数の噴出孔67を設けた有底筒68とから成るほぼ2重管状に構成されている。噴出したH_2は、まず、H_2噴出ノズル66に排圧の動圧によって流入する排気と混合し、有底筒68の内筒から外筒に噴出し、内外筒の間を流れる排気により更に混合する。このように2段階の混合過程を経るのでほぼH_2と排気が完全に均一混合することができる。

【0050】内外筒の大きさ（直径、または断面積）は混合に大きく影響し、内筒が小さいとほとんどの排気は外筒を流れ、十分動圧を利用できない。図17、図18に於いて内外筒の直径比はD／d（外筒／内筒）は3～1.7程度が有効で2付近が最良である。

【0051】上記構成からなる第3実施例は、混合が良好となり、モノリスタイプであってもペレットタイプ同様の浄化率を得ることができる。同一浄化率において供給H_2量を30～60％節約することができるので、H_2発生に要する燃料を少なくでき、エンジンの出力や燃費への影響を軽減できる。

【0052】例えば、1.61のリーンバーンガソリンエンジンにおいて通常の運転域代表点で評価すると、エンジン回転数2000rpm、トルク40Nm、この時のNO_x放出量0.441／min、このNO_xをH_2還元で浄化するのに要するH_2流量は、0.661／min。0.661／minのH_2を発生させるのにH_2発生器への燃料は0.331／minの燃料蒸気になる（メタノールの場合）。

【0053】D／d＝2である図17、図18に示す装置によって混合促進を行えば、H_2の供給量はNO_xと等量の0.441／min程度で済み、燃料は0.221／minの蒸気0.221／minの蒸気に低下する。即ち0.111／minの節約となる。

【0054】

【第4実施例】前記実施例においてゼオライト系触媒を用い、水素発生器によって水素を発生させ、H_2をゼオライト系触媒の入口に供給しH_2によるNO_x還元を行えば排気中に高濃度のO_2が存在していても大きなNO_x浄化率が得られる。

【0055】しかし、従来のNO_x触媒、例えば三元触媒、Cu－ゼオライト系触媒に比べると低温の反応であって、従来の触媒がSV値（通過ガス流量1／hrと触媒体積1の比）50,000～100,000を使っているのに比べると反応速度の関係からより小さなSV（例えば10,000～60,000）を使わなくてはならない。このシステムを車載する場合、本システムの改質触媒コンバータは入口ガス温度から排気系統の下流、例えば排気マフラー付近になる。しかるに車輌に於いては車輌構造上SV値の大きい（コンバータの大きさの大きい）改質触媒コンバータを設置する場所になっており、すべての車輌へは適用し難い。

【0056】本第4実施例は、改質触媒コンバータの設置を容易にするため、リーンNO_x触媒をマフラーに内蔵させコンパクト化を計るためのマフラー構造およびマフラーに触媒を内蔵させても温度条件からNO_x浄化を可能とするものである。

【0057】すなわち、第4実施例の構成は、図20、図21に示すように、排気マフラー80にリーンNO_x触媒82を内蔵させるとNO_xコンバータと、排気マフラーを直列に配置することなく片方で済むため、配置スペース的に極めて有利となる。図20、図21に排気マフラー80にモノリス触媒82（Pt－ゼオライト系）を内蔵した消音効果を持たせた改質触媒コンバータ83を示す。

【0058】改質触媒コンバータ83の上流よりH_2を混入混合された排気が矢印方向より流入し、ミキシングプレート84に衝突し、このミキシングプレート84の大小複数の流通孔85を通過して排気とH_2が十分混合しながらモノリス触媒82に流入する。ミキシングプレート84には排気流速最大になる中心部に流通孔85が設けられていないので、H_2がモノリス中心部に集中することはない。ミキシングプレート84の流通孔85は、大小それぞれ直径を異にして複数配列されているので通過流速が異なり、ガスの攪拌が起こると共に干渉によって消音効果を奏する。

【0059】ところで、排気マフラーはエンジン排気系統の最後尾に配置されるのが一般的で、排気マフラーの入口ガス温度は途中で冷却されるので低くなる。入口温度が最も高いエンジンの最高回転数最大馬力時でも150～200℃であり、通常使用頻度の高い運転条件では100～150℃程度である。

【0060】従来の三元触媒やCu－ゼオライト系のリーンNO_x触媒では300～400℃以上でないと十分な反応が期待できないからマフラー内に触媒を内蔵させることはできない。前記実施例において、H_2による還元を行えば低温で浄化できることを示したが、温度は150～300℃程度であって排気マフラーの入口温度と比べればやや高い温度範囲にある。

【0061】本発明者等は、O_2共存下でH_2を供給するNO_x低減触媒の活性について触媒成分として何を選定するべきかを種々実験的に検討した。その結果、Pd、Rhは活性が全くなく、Cuは活性が弱く、Ptが高い活性を示すことを見出した。ただし、Ptは高分散である必要があり、そのためには高比表面積（少なくとも100m^2／g以上）を有するアルミナ、シリカ、ゼオライト等の担体が必要である。

【0062】更に、本発明者等は、NO_x低減のリーンNO_x触媒およびH_2混合以前に行うべき前処理について種々に検討を行った。その結果を図19に示す。エンジンの排気にH_2を混合してNO_x低減のリーンNO_x

触媒（Ｐｔ系）に導くと図１９中、曲線Ｂに示すように活性の最高点は２５０℃付近にある。

【００６３】アフターバーナ、リアクタ、三元触媒、酸化触媒等をエンジンマニホールド付近に設け、ＣＯ、ＨＣを酸化し予め低減除去した後にH_2を供給しＮＯｘ低減の改質触媒コンバータに導くと図１９中曲線Ａに示すように活性温度が低温側にシフトし、１００～１５０℃で高い活性を示すことを新たに見出した。

【００６４】この温度は、排気マフラーの入口温度と一致し、排気マフラー８０内にＰｔ－ゼオライト系の還元触媒８０を内蔵することにより初めて可能ならしめた。更に、ＨＣ、ＣＯを除去した後にリーンＮＯｘ触媒によるＮＯｘ浄化を行った方が浄化率も改善でき、ＨＣ－O_2の不完全な反応から触媒上にススを形成することもない実用上優れた作用効果を奏する。

【００６５】更にモノリス触媒８２の後に干渉チューブＥｘ１を設置することにより消音効果をより良好にしている。図２２は図２０、図２１と同様の作用効果を奏するもので、ミキサー部の形態を前記ミキシングプレートと異にし、中空筒状部材であるミキシングパイプ８６とした点が異なる。上記構成からなる第４実施例は、改質触媒コンバータ８３と排気マフラー８０が一体化構成とすることができるので、コンパクトとなり車載性が良好となる実用的効果を奏すると共に、全運転範囲で高いＮＯｘ浄化率を維持できる優れた効果を奏する。

【図面の簡単な説明】

【図１】本発明の実施例の基本構成を示す構成図

【図２】空燃比と燃料経済性の関係を示す線図

【図３】リーンバーンエンジンの燃費とＮＯｘの関係を示す線図

【図４】リーンＮＯｘ触媒の特性を示す線図

【図５】H_2供給率とＮＯｘ浄化率の関係を示す線図

【図６】本発明の第１実施例装置の概要を示す構成図

【図７】第１実施例装置におけるH_2発生器の断面図

【図８】第１実施例装置におけるその他のH_2発生器の要部を拡大して示す構成図

【図９】本発明の第２実施例装置の概要を示す構成図

【図１０】本発明の第３実施例装置の概要を示す構成図

【図１１】第３実施例装置に関してＮＯｘ浄化率の関係を示す線図

【図１２】第３実施例装置に関してペレットタイプの触媒構成を示す概要図

【図１３】第３実施例装置に関してモノリスタイプの触媒構成を示す概要図

【図１４】本発明の第３実施例装置の概要を示す縦断面図

【図１５】本発明の第３実施例装置の概要を示す横断面図

【図１６】本発明の第３実施例装置の概要を示す概要図

【図１７】本発明の第３実施例装置のその他の例を示す縦断面図

【図１８】本発明の第３実施例装置のその他の例を示す横断面図

【図１９】本発明の第４実施例に関してＮＯｘ浄化率状況を示す線図

【図２０】本発明の第４実施例装置の概要を示す縦断面図

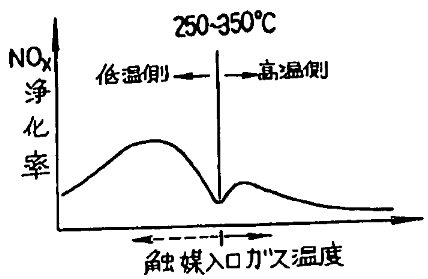
【図２１】本発明の第４実施例装置の概要を示す横断面図

【図２２】本発明の第４実施例装置のその他の構成を示す縦断面図

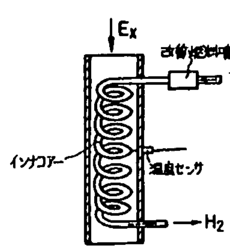
【符号の説明】

Ｅ、E_1	エンジン
１、１１	H_2発生器
３、１３、８０	消音器
１２、６０	還元触媒
９	酸化触媒
５	吸入空気量センサ
６	ＮＯｘセンサ
７	コントロール電源
１０	ミキサー

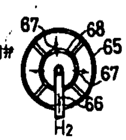
【図４】



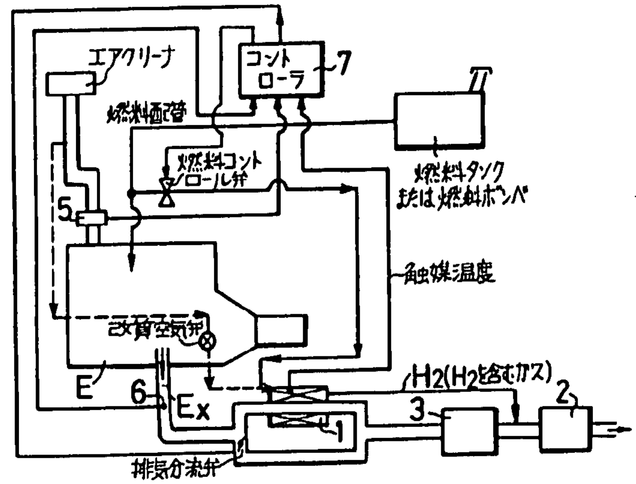
【図７】



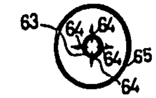
【図１８】



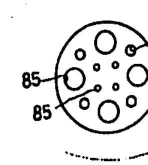
【図１】



【図１５】



【図２１】



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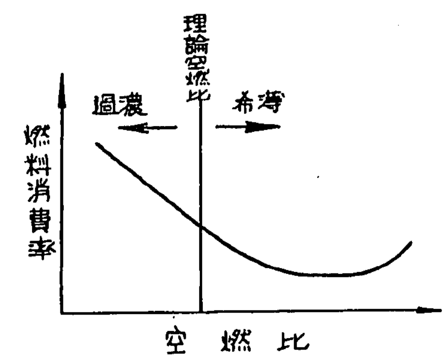

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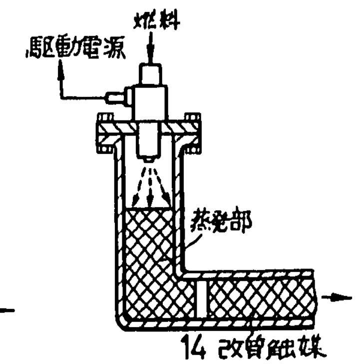
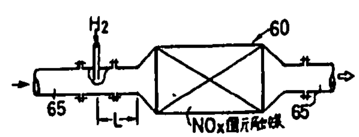
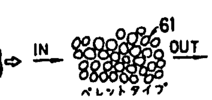


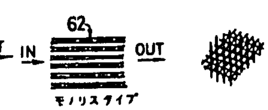
【図１０】



【図１２】



【図１３】



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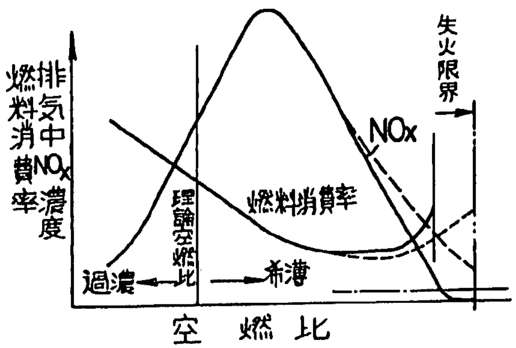

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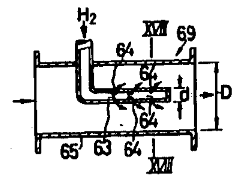

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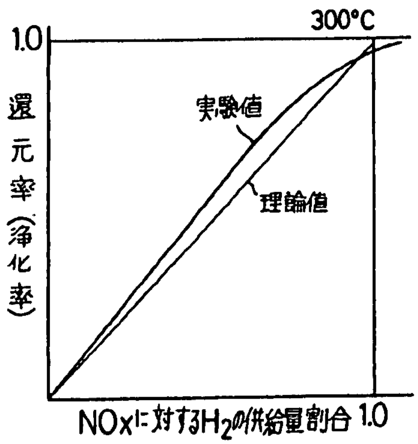

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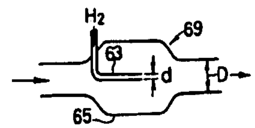

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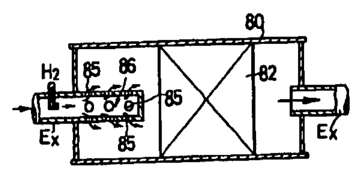

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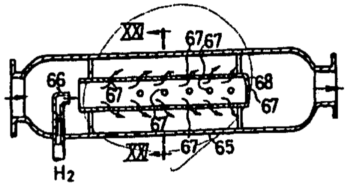

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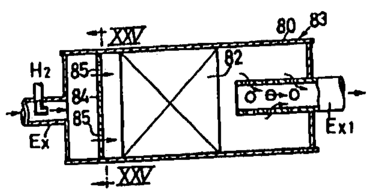

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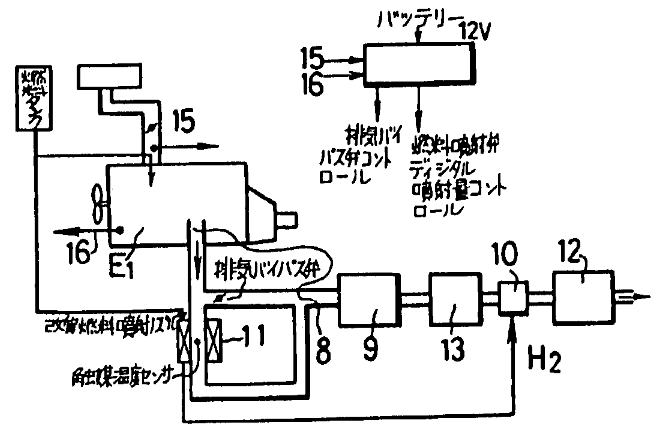

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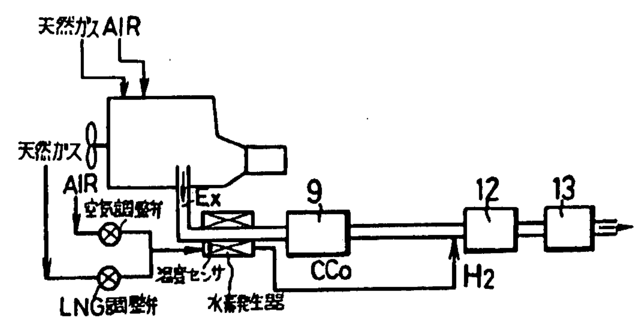

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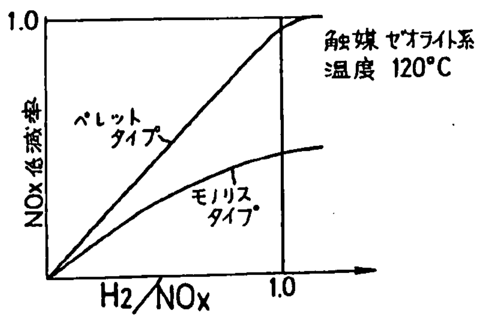

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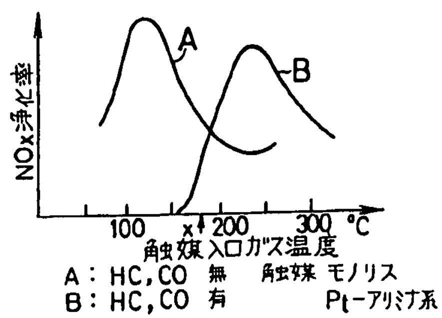

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